

ACCUMULATION RATE OF BOUND STATES OF DIPOLES IN GRAPHENE

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ABSTRACT. We prove that the bound state energies of the two-dimensional massive Dirac operator with dipole type potentials accumulate with exponential rate at the band edge. In fact we prove a corresponding formula of De Martino et al [3].

1. INTRODUCTION

Recently the bound state problem for strained graphene with a dipole became of interest in the physics literature (De Martino et al [3]). This is described effectively by a two-dimensional massive Dirac operator D_ϕ with a dipole potential ϕ , i.e.,

$$(1) \quad D_\phi := \sigma \cdot p + \sigma_3 - \phi$$

with $\sigma := (\sigma_1, \sigma_2)$ (the first two Pauli matrices), $p := (1/i)(\partial_1, \partial_2)$, and real valued potential

$$(2) \quad \phi := d + s$$

where

$$d(x) := \begin{cases} \mathfrak{d} \cdot \frac{x}{|x|} |x|^{-2} & |x| > 1 \\ 0 & |x| \leq 1 \end{cases}$$

with $\mathfrak{d} \in \mathbb{R}^2$ is the potential of a pure point dipole at the origin outside the ball of radius one around the origin. Without loss of generality, we can – and will from now on – pick $\mathfrak{d} := (b, 0)$ with $b > 0$, i.e., a multiple of the unit vector along the first coordinate axis. The potential s will be the – possibly – singular part of the potential that is short range in the sense that $-\Delta - s$ has only finitely many bound states.

It is folklore that the discrete spectrum of D_ϕ would be infinite, if ϕ had a non-vanishing Coulomb tail. This is also true for its three dimensional analogue. However, dimension two and three differ in the case of a dipole potential: whereas in three dimensions there are – for small coupling constant – only finitely many eigenvalues in the gap [1], $\sigma_d(D_\phi)$ is always infinite in two dimensions. This has been predicted by De Martino et al [3] and proved in [2]. In fact, De Martino et al even derived a formula for the accumulation rate of the eigenvalues at the band edge. The purpose of this paper is to prove their formula. To formulate our result we need some notation:

Definition 1. *We write*

- $N_I(A)$ for the number of eigenvalues of a linear operator A in $I \subset \mathbb{C}$ – counting multiplicity,
- M_b for the – rescaled – Mathieu operator with periodic boundary conditions at 0 and 2π defined by

$$(3) \quad (M_b g)(\varphi) = -g''(\varphi) - b \cos(\varphi)g(\varphi),$$

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- $B_{i\nu}$ for the Bessel operator with imaginary order defined by

$$(4) \quad (B_{i\nu}f)(z) = -f''(z) - \frac{1}{z}f'(z) - \frac{\nu^2}{z^2}f(z).$$

Remark 1. The lowest eigenvalue a_0 of the rescaled Mathieu operator M_b fulfills the transcendental equation (McLachlan [8, 3.11.(8)])

$$(5) \quad a_0 = \frac{1}{4} \left(-\frac{\frac{1}{2} \left(\frac{b}{4}\right)^2}{1 - \frac{1}{4} \frac{a_0}{4}} - \frac{\frac{1}{64} \left(\frac{b}{4}\right)^2}{1 - \frac{1}{16} \frac{a_0}{4}} - \frac{\frac{1}{576} \left(\frac{b}{4}\right)^2}{1 - \frac{1}{36} \frac{a_0}{4}} - \dots \right),$$

in particular a_0 is negative for all b (McLachlan [8, 3.25. diagram]).

The above notation allows to formulate our main result.

Theorem 1. Assume that $\phi = d + s$ is real valued with d as in (2), and that the singular part s is relatively compact with respect to D_0 and its negative part s_- even fulfills

$$\int_{\mathbb{R}^2} s_-(x) \log(2 + |x|) dx + \int_0^1 s_-^*(\pi t) |\log(t)| dt < \infty$$

and also

$$\int_{\mathbb{R}^2} s^2(x) \log(2 + |x|) dx + \int_0^1 (s^2)^*(\pi t) |\log(t)| dt < \infty.$$

Then

$$(6) \quad \lim_{E \nearrow 1} \frac{N_{(-E, E)}(D_\phi)}{|\log(1 - E)|} = \frac{1}{\pi} \text{tr} \sqrt{M_{2b-}}.$$

Before we embark on the proof we make a few comments:

Domain: Our condition on the potential ϕ assures that D_ϕ is self-adjoint on $H^1(\mathbb{R}^2 : \mathbb{C}^2)$ and that the essential spectrum of D_ϕ is $\mathbb{R} \setminus (-1, 1)$.

Electric Potentials: One possible realization of ϕ is to think of it as the electric potential of some sufficiently smooth and localized charge density ρ , i.e.,

$$\phi(x) = \int_{\mathbb{R}^3} \frac{\rho(\mathfrak{y}) d\mathfrak{y}}{|(x, 0) - \mathfrak{y}|}$$

with vanishing monopole moment, i.e., $\int_{\mathbb{R}^3} \rho = 0$ and to assume that the dipole moment $\int_{\mathbb{R}^3} \mathfrak{y} \rho(\mathfrak{y}) d\mathfrak{y}$ of ρ points in the direction of the first coordinate axis. (See, e.g., Jackson [5, Chapter 4] for a discussion of multipole expansions of potentials. Note that we extend the vector $x \in \mathbb{R}^2$ by zero to a vector $\mathfrak{x} = (x, 0) \in \mathbb{R}^3$.)

Instead of three dimensional densities, we could also allow for densities $\rho(\mathfrak{x}) = \rho^{(2)}(x) \delta(x_3)$ that are confined to the electron plane.

Point Charges: Our hypothesis excludes point charges located directly in the graphene sheet, i.e., the plane in which the electrons move. Although it is certainly possible to treat a finite number of such singularities with subcritical coupling constants, i.e., less than $1/2$, this would require an analysis of the compactness properties of D_ϕ^2 when restricted to functions in a ball containing the singularities of ϕ . We refrain from embarking on this subtlety, since it is irrelevant for the long range behavior of the potential which determines the asymptotic behavior of the eigenvalues.

2. PROOF OF THE MAIN THEOREM

Intuitively the long range behavior determines the asymptotic behavior of the eigenvalues. This motivates to prove the following lemma including pure dipole potentials.

Lemma 1. *For real $a, b \in \mathbb{R}$, $R \in \mathbb{R}_+$, $A := \{x \in \mathbb{R}^2 \mid |x| > 1\}$. Set*

$$H_{a,b} := -\Delta - \frac{a + bx_1/|x|}{|x|^2}$$

on $H_0^2(A)$ or $H^2(A)$, i.e., the operator with Dirichlet respectively Neumann boundary conditions on the boundary of A . Then

$$(7) \quad \lim_{E \nearrow 0} \frac{N_{(-\infty, E)}(H_{a,b})}{|\log(|E|)|} = \frac{1}{2\pi} \text{tr} \sqrt{(M_b - a)_-}.$$

Note that the theorem is only nontrivial, if the sum of the lowest Mathieu eigenvalue $-\mu$ and $-a$ is negative. This, however, is the case for $a = 0$, since the first Mathieu eigenvalue is always negative (McLachlan [8]).

We know of two ways proving the lemma. The first relies on Dirichlet-Neumann bracketing; it adapts an argument that Kirsch and Simon [7] developed for direction independent pure $1/r^2$ -potentials to the case of dipole potentials (direction dependent decay (!)). (See Rademacher [9] for details.) The method presented here is somewhat different. As we will see in the proof, the essential ingredient is the short range behavior of modified Bessel functions with imaginary order which – we feel – is more direct. Moreover it is closer to the derivation by De Martino et al [3].

We begin with the proof of the Lemma.

Proof. We solve $H_{a,b}\psi = -\lambda\psi$ by separating variables, i.e., we make the ansatz $\psi(x) = f(r)g(\varphi)$ in spherical coordinates $x_1 = r \cos(\varphi)$ and $x_2 := r \sin(\varphi)$ and require periodic boundary conditions for g , i.e., $g(\varphi) = g(\varphi + 2\pi)$. Then g is an eigenfunction of the Mathieu operator, i.e., $M_b g = -\mu g$, and f is an eigenfunction of the Bessel operator $B_{i\sqrt{a+\mu}} f = -\lambda f$ which we need to solve with Dirichlet respectively Neumann boundary condition at 1 and Dirichlet condition at infinity, depending on whether we solve the problem in $H_0^2(A)$ or $H^2(A)$.

As mentioned above, the Mathieu operator M_b has for all positive b at least one negative eigenvalue. Because of the boundary condition at infinity we have that the only solutions of (4) are

$$(8) \quad f(r) = K_{i\sqrt{\mu+a}}(\sqrt{\lambda}r).$$

(Note that the functions $I_{i\sqrt{\mu+a}}(\sqrt{\lambda}\cdot)$ and $K_{i\sqrt{\mu+a}}(\sqrt{\lambda}\cdot)$ are two linearly independent solutions of Bessel's equation. However, $I_{i\sqrt{\mu+a}}(\sqrt{\lambda}\cdot)$ is excluded because of its exponential blow up at infinity (Watson [12, Chapter 7.23, Formula (2)]).

Next we note that, since the change from Dirichlet to Neumann boundary condition at 1 is a perturbation of rank one for each fixed eigenvalue of the Mathieu equation, we merely need to consider the Dirichlet case. Thus we are interested in finding the maximal number of nodes that a function $K_{i\sqrt{\mu+a}}(\sqrt{\lambda}\cdot)$ can have for fixed $\mu + a$, assuming that $K_{i\sqrt{\mu+a}}(\sqrt{\lambda}) = 0$ and any $-\lambda \leq E$, i.e.,

$$(9) \quad \left| \{r \geq 1 \mid K_{i\sqrt{\mu+a}}(\sqrt{\lambda}r) = 0, -\lambda \leq E\} \right|.$$

If $a + \mu \leq 0$, the operator $B_{\sqrt{|a+\mu|}}$ has no eigenfunctions and the claim is trivially true, i.e., we may assume that $a + \mu > 0$. Thus, we need to find the maximal n such that

$$(10) \quad \sqrt{-E} \leq k_{\sqrt{\mu+a}, n} = O(\exp(-(n\pi - \phi_{\sqrt{\mu+a}})/\sqrt{\mu+a}))$$

where $k_{\sqrt{\mu+a},n}$ denotes the zeros of $K_{i\sqrt{\mu+a}}(\sqrt{\lambda}\cdot)$ using their asymptotic expansion (see (24)). Taking the logarithm and dividing by $|\log(-E)|$ yields

$$(11) \quad n/|\log(-E)| \rightarrow \frac{\sqrt{\mu+a}}{2\pi}$$

as $E \nearrow 0$. Since the lower bound can deviate by at most one, this is covered as well. \square

Next we turn to the proof of the theorem:

Proof. We begin by noting that the operator D_ϕ is a relatively compact perturbation of the free Dirac operator D_0 . This implies that D_ϕ has only eigenvalues of finite multiplicity in $(-1, 1)$, the spectral gap of D_0 . Furthermore those eigenvalue can only accumulate at -1 or 1 . Thus, by the spectral theorem

$$(12) \quad N_{(-1,1)}(D_\phi) = N_{(-\infty,0)}(D_\phi^2 - 1).$$

which reduces the problem to study the negative eigenvalues of a relatively compact perturbation of the Laplacian, since

$$(13) \quad D_\phi^2 - 1 = -\Delta + \phi^2 + (\sigma \cdot p)\phi + \phi(\sigma \cdot p) - 2\sigma_3\phi.$$

The Schwarz inequality – followed by the geometric-arithmetic mean inequality – yields for any positive ϵ

$$(14) \quad |2\Re(\psi, \epsilon(\sigma \cdot p)(\epsilon^{-1}\phi)\psi)| \leq \epsilon^2 \|p\psi\|^2 + \epsilon^{-2} \|\phi\psi\|^2.$$

Thus

$$(15) \quad D_\phi^2 - 1 \leq (1 + \epsilon^2)p^2 + (1 + \epsilon^{-2})\phi^2 - 2\sigma_3\phi$$

and

$$(16) \quad D_\phi^2 - 1 \geq (1 - \epsilon^2)p^2 + (1 - \epsilon^{-2})\phi^2 - 2\sigma_3\phi.$$

Note the lower bound (16) is bounded from below for $\epsilon \in (0, 1)$, since both ϕ and ϕ^2 are relative compact perturbations of p^2 .

Both right hand sides of (15) and (16) separate in two independent one component operators, since σ_3 is diagonal. We shall focus on the first component. (As the proof shows the second component will give the same answer because of the symmetry of the pure dipole part.) We write

$$(17) \quad (1 \pm \epsilon^2)h_\pm := (1 \pm \epsilon^2) \left(p^2 + \epsilon^{-2}\phi^2 - \frac{2}{(1 \pm \epsilon^2)}\phi \right)$$

for the first components of the right hand side of (15) and (16). The task is now to estimate $N_{(-\infty, E)}(h_+)$ from below and $N_{(-\infty, E)}(h_-)$ from above as $E \nearrow 0$. We begin with the lower bound to $N_{(-\infty, 0)}(h_+)$ and write in the spirit of (28)

$$(18) \quad h_\pm = -\Delta + V_\pm + W_\pm,$$

$$(19) \quad V_\pm := -2(1 \pm \epsilon^2)^{-1}d,$$

$$(20) \quad W_\pm := \epsilon^{-2}\phi^2 - 2(1 \pm \epsilon^2)^{-1}s.$$

(Note that the indices \pm at h , V , and W , are just indices motivated by the signs in (15) and (16) and not to the positive part and negative part of an operator as elsewhere in the paper.) Thus, by (28)

$$(21) \quad \limsup_{E \nearrow 0} \frac{N_{(-\infty, E)}(h_+)}{|\log(|E|)|} \geq \limsup_{E \nearrow 0} \frac{N_{(-\infty, E)}(-\Delta - (1 - \epsilon)V_+)}{|\log(|E|)|},$$

since $N_{(-\infty, E)}(-\Delta + (1 - \epsilon)\epsilon^{-1}W_+) \leq N_{(-\infty, 0)}(-\Delta + (1 - \epsilon)\epsilon^{-1}W_+) < \infty$ by (25) and thus vanishes when divided by $\log(|E|)$ as $E \nearrow 0$. Finally, we take ϵ to zero and get

$$(22) \quad \limsup_{E \nearrow 0} \frac{N_{(-\infty, E)}(h_+)}{|\log(|E|)|} \geq \limsup_{E \nearrow 0} \frac{N_{(-\infty, E)}(-\Delta - 2d)}{|\log(|E|)|} \\ \geq \limsup_{E \nearrow 0} \frac{N_{(-\infty, E)}\left((- \Delta - 2d)|_{H_0^2(\{x \in \mathbb{R}^2 \mid |x| > 1\})}\right)}{|\log(|E|)|} = \frac{1}{2\pi} \text{tr} \sqrt{M_{2b-}}$$

using (7) in the last step. Repeating the argument for the second component yields the same result. Adding the results for both components gives the claimed upper bound.

We now turn to the upper bound. We use (16) to estimate the operator from below and thus, the number of eigenvalues from above. Again the operator decouples into two one-component operators and we are left with the task to compute twice the number of eigenvalues of h_- below $-E$ as remarked already above. Next we use (27) to estimate from above and note – similarly to the lower bound – that the W_- part does not contribute. As above we now get

$$(23) \quad \limsup_{E \nearrow 0} \frac{N_{(-\infty, E)}(h_-)}{|\log(|E|)|} \leq \limsup_{E \nearrow 0} \frac{N_{(-\infty, E)}(-\Delta - 2d)}{|\log(|E|)|} \\ \leq \limsup_{E \nearrow 0} \frac{N_{(-\infty, E)}\left((- \Delta - 2d)|_{H^2(\{x \in \mathbb{R}^2 \mid |x| > 1\})}\right)}{|\log(|E|)|} = \frac{1}{2\pi} \text{tr} \sqrt{M_{2b-}}$$

where we estimated by the Neumann operator and used (7) again. Doubling the bound because of the two components gives the desired result. \square

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APPENDIX A. SOME AUXILIARY FORMULAE ABOUT THE ASYMPTOTIC OF BESSEL FUNCTIONS

Dunster [4, Formula 2.8] offers the asymptotic formula

$$(24) \quad k_{\nu, n} = 2 \exp(-(n\pi - \phi_\nu)/\nu) \left(1 + \frac{\exp(-2(n\pi - \phi_\nu)/\nu)}{1 + \nu^2} + O(\exp(-4(n\pi - \phi_\nu)/\nu)) \right)$$

as $n \rightarrow \infty$ for the n -th zero (counting from the right) of the modified Bessel function $K_{i\nu}$ for fixed imaginary order. Here

$$\phi_\nu := \arg(\Gamma(1 + i\nu)).$$

APPENDIX B. BOUNDS ON THE NUMBER OF EIGENVALUES OF SCHRÖDINGER OPERATORS IN TWO DIMENSIONS

Since negative potentials in one and two dimensions generate always at least one bound state with negative energy, the standard Lieb-Cwikel-Rosenblum bounds cannot hold. Following earlier works in the physics literature (see Khuri, Martin, and Wu [6]), Shargorodsky [11, Theorem 4.3] showed that there is a positive constant C such that for all V the number $N_-(V) := N_{(-\infty, 0)}(-\Delta + V)$ of negative eigenvalues of $-\Delta + V$ is bounded by

$$(25) \quad N_-(V) \leq C \left(\int_{\mathbb{R}^2} V_-(x) \log(2 + |x|) dx + \int_0^1 V_-^*(\pi t) |\log(t)| dt \right) + 1$$

where the subscript V_- denotes the negative part of V and V_-^* the spherically symmetric rearrangement of V_- .

APPENDIX C. KNOWN BOUNDS ON THE NUMBER OF EIGENVALUES OF SUMS OF OPERATORS

The number of eigenvalues of the sum of two self-adjoint operators A and B that are bounded by below and having $\inf \sigma_{\text{ess}}(A) = \inf \sigma_{\text{ess}}(B) = 0$ can be estimated by the sum of the number of eigenvalues of each single operator, i.e., for $E < 0$

$$(26) \quad N_{(-\infty, E)}(A + B) \leq N_{(-\infty, E)}(A) + N_{(-\infty, E)}(B).$$

This formula is a consequence of the minimax theorem and was proved by Kirsch and Simon [7, Proposition 4] resp. Reed and Simon [10, p.274, Formula (125)]. In particular this formula applies for Schrödinger operators of the form $H = -\Delta + V + W$ with potentials V, W in \mathbb{R}^2 such that $\inf \sigma_{\text{ess}}(H) = 0$ [7, Proposition 5 (i)]. We obtain for $\epsilon > 0$ and $E < 0$

$$(27) \quad N_{(-\infty, E)}(-\Delta + V + W) \leq N_{(-\infty, E)}(-\Delta + \frac{1}{1-\epsilon}V) + N_{(-\infty, E)}(-\Delta + \frac{1}{\epsilon}W).$$

This estimate leads to the lower bound

$$(28) \quad N_{(-\infty, E)}(-\Delta + V + W) \geq N_{(-\infty, E)}(-\Delta + (1-\epsilon)V) - N_{(-\infty, E)}(-\Delta - \frac{1-\epsilon}{\epsilon}W)$$

for the number of eigenvalues of H [7, Proposition 5 (ii)].

REFERENCES

- [1] D. I. Abramov and I. V. Komarov. Weakly bound states of a charged particle in a finite-dipole field. *Theoretical and Mathematical Physics*, 13(2):1090–1098, 1972.
- [2] Jean-Claude Cuenin and Heinz Siedentop. Dipoles in graphene have infinitely many bound states. *Journal of Mathematical Physics*, 55(12):122304, 2014.
- [3] Alessandro De Martino, Denis Klöpfer, Davron Matrasulov, and Reinhold Egger. Electric-dipole-induced universality for Dirac fermions in graphene. *Physical Review Letters*, 112(18):186603, 2014.
- [4] T. M. Dunster. Bessel functions of purely imaginary order, with an application to second-order linear differential equations having a large parameter. *SIAM J. Math. Anal.*, 21(4):995–1018, 1990.
- [5] John David Jackson. *Classical Electrodynamics*. John Wiley & Sons, Inc., New York-London-Sydney, first edition, 1962.
- [6] N. N. Khuri, A. Martin, and T.-T. Wu. Bound states in n dimensions (especially $n = 1$ and $n = 2$). *Few-Body Systems*, 2002.
- [7] Werner Kirsch and Barry Simon. Corrections to the classical behavior of the number of bound states of Schrödinger operators. *Ann. Physics*, 183(1):122–130, 1988.
- [8] N. W. McLachlan. *Theory and Application of Mathieu Functions*. Oxford, at the Clarendon Press, 1947.
- [9] Simone Rademacher. Energieniveaus von Dipolen in Graphen. Master’s thesis, Mathematisches Institut der Ludwig-Maximilians-Universität München, Theresienstraße 39, 80333 München, May 2015.
- [10] Michael Reed and Barry Simon. *Methods of Modern Mathematical Physics*, volume 4: Analysis of Operators. Academic Press, New York, 1 edition, 1978.
- [11] Eugene Shargorodsky. On negative eigenvalues of two-dimensional Schrödinger operators. *Proc. London Math. Soc.*, 108(3):441–483, 2013.
- [12] G. N. Watson. *A Treatise on the Theory of Bessel Functions*. Cambridge University Press, Cambridge, 1st edition, 1922.

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